

CLAIMS

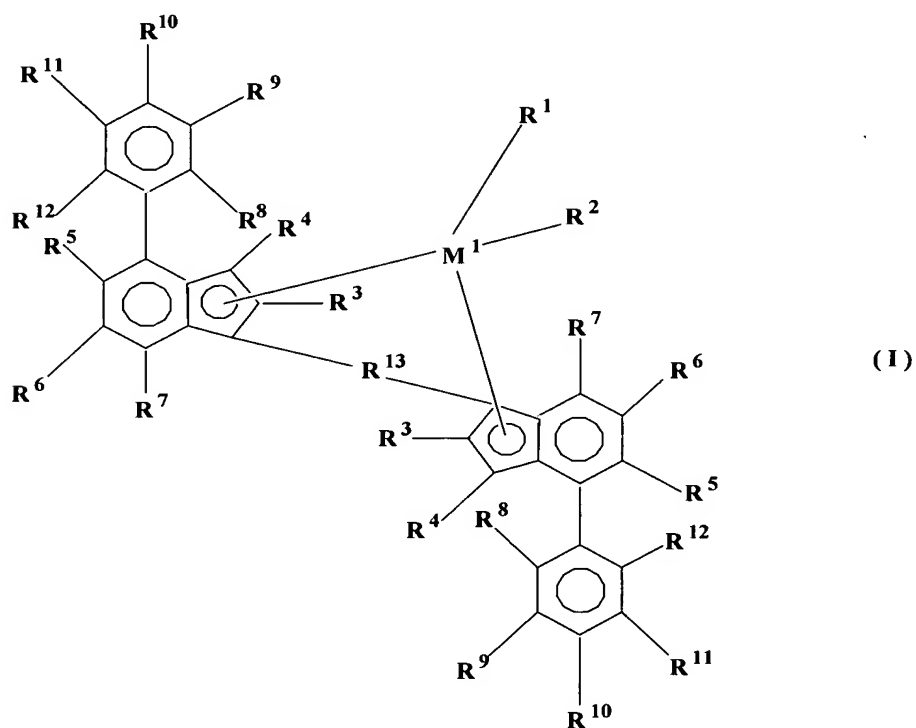
WHAT IS CLAIMED IS:

1. A process of preparing a polymer composition that includes a branched crystalline diene-modified polypropylene random terpolymer, comprising:
contacting a metallocene catalyst compound with a polymerization medium that includes at least a propylene monomer, a first diene monomer, and a second diene monomer, in which the first diene monomer and the second diene monomer are different non-conjugated dienes, each having 5 or more carbon atoms; and
conducting polymerization of the monomers in the presence of the metallocene catalyst compound for a time sufficient to provide a branched crystalline diene-modified polypropylene random terpolymer that includes monomeric units derived from each of the monomers, and having from 0.0 wt% to 2.0 wt% ethylene and a heat of fusion of 30 J/g or more.
2. A process of preparing a polymer composition that includes a branched crystalline diene-modified polypropylene random terpolymer, comprising:
contacting a metallocene catalyst compound with a polymerization medium that includes at least a propylene monomer, an α , internal non-conjugated diene monomer, and a α , ω non-conjugated diene monomer; and
conducting polymerization of the monomers in the presence of the metallocene catalyst compound for a time sufficient to provide a branched crystalline diene-modified polypropylene random terpolymer that includes monomeric units derived from each of the monomers, and having from 0.0 wt% to 2.0 wt% ethylene and a heat of fusion of 30 J/g or more.
3. The process of claim 1, in which the first diene monomer is an α , internal diene.

4. The process of claim 1, in which the second diene monomer is an α , ω diene.
5. The process of claim 1, in which the first diene monomer is an α , internal non-conjugated diene monomer; and the second diene monomer is an α , ω non-conjugated diene monomer.
6. The process of claim 1, in which either the first diene monomer or the second diene monomer has an internal double bond comprising a di-substituted vinyl group or a tri-substituted vinyl group.
7. The process of claim 1, in which either the first diene monomer or the second diene monomer has an internal double bond comprising a di-substituted vinyl group or a tri-substituted vinyl group having one or more methyl group substituents.
8. The process of claim 1, on which the first diene monomer is an α , internal non-conjugated diene monomer having an internal double bond comprising a tri-substituted vinyl group having two methyl group substituents.
9. The process of claim 1, in which the second diene monomer is an α , ω diene comprising unsubstituted 1,4-pentadiene; 1,5-hexadiene; 1,6-heptadiene; 1,7-octadiene; 1,8-nonadiene; or 1,9-decadiene.
10. The process of claim 1, in which either the first diene monomer or the second diene monomer comprising substituted 1,4-pentadiene; 1,5-hexadiene; 1,6-heptadiene; 1,7-octadiene; 1,8-nonadiene; or 1,9-decadiene.
11. The process of claim 1, in which the second diene monomer comprises 2-methyl-1,5-hexadiene.

12. The process of claim 1, in which the first diene monomer comprises 2-methyl-1,5-hexadiene or 7-methyl-1,6-octadiene.
13. The process of claim 1, in which the amount of the first diene monomer is greater than the amount of the second diene monomer.
14. The process of claim 1, in which the first diene monomer is an α , internal non-conjugated diene monomer; the second diene monomer is an α , ω non-conjugated diene monomer; and the amount of the first diene monomer is greater than the amount of the second diene monomer.
15. The process of claim 1, in which the polymerization medium includes 50 mol% or more propylene monomers, 10 mol% or less α , internal non-conjugated diene monomers, and 1 mol% or less α , ω non-conjugated diene monomers.
16. The process of claim 1, in which the metallocene catalyst compound is or includes a substituted or unsubstituted silyl-bridged or ethylene-bridged bis-indenyl metallocene.
17. The process of claim 1, in which the metallocene compound comprises a bridged metallocene compound having at least two indenyl rings or derivatives of indenyl rings, each ring being substituted at the 2 position.
18. The process of claim 1, in which the metallocene compound comprises a bridged metallocene compound having at least two indenyl rings or derivatives of indenyl rings, each ring being substituted at the 2 and 4 positions.
19. The process of claim 1, in which the metallocene compound comprises supported dimethylsilylbis(2-methyl-4-phenyl-1-indenyl)zirconium dimethyl.

20. The process of claim 1, in which the metallocene includes a dimethylanilinium tetrakis (perfluorophyl) boron activator.
21. The process of claim 1, in which the supported metallocene includes a methlyaluminoxane activator.
22. The process of claim 1, in which the metallocene compound is represented by the formula:



wherein:

M^1 is selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten;

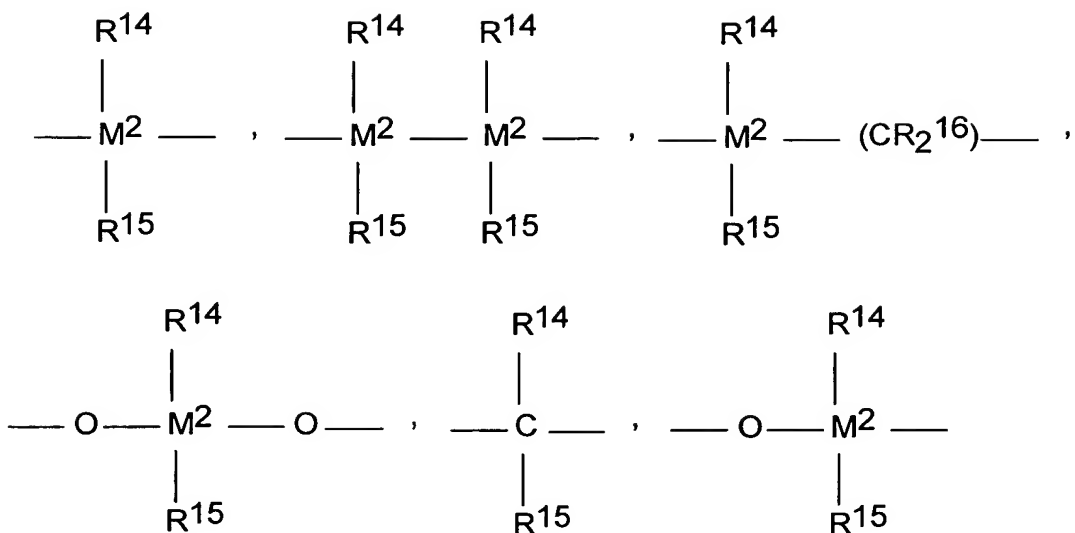
R^1 and R^2 are identical or different, and are one of a hydrogen atom, a C_1 - C_{10} alkyl group, a C_1 - C_{10} alkoxy group, a C_6 - C_{10} aryl group, a C_6 - C_{10} aryloxy group, a C_2 - C_{10} alkenyl group, a C_2 - C_{40} alkenyl group, a C_7 - C_{40} arylalkyl

group, a C₇-C₄₀ alkylaryl group, a C₈-C₄₀ arylalkenyl group, an OH group or a halogen atom; R¹ and R² may also be joined together to form an alkanediyl group or a conjugated C₄-C₄₀ diene ligand which is coordinated to M¹ in a metallocyclopentene fashion; R¹ and R² may also be identical or different conjugated dienes, optionally substituted with one or more hydrocarbyl, tri(hydrocarbyl)silyl groups or hydrocarbyl, tri(hydrocarbyl)silylhydrocarbyl groups, said dienes having up to 30 atoms not counting hydrogen and forming a π complex with M, examples include 1,4-diphenyl-1,3-butadiene, 1,3-pentadiene, 2-methyl-1,3-pentadiene, 2,4-hexadiene, 1-phenyl-1,3-pentadiene, 1,4-dibenzyl-1,3-butadiene, 1,4-ditolyl-1,3-butadiene, 1,4-bis(trimethylsilyl)-1,3-butadiene, and 1,4-dinaphthyl-1,3-butadiene;

Each R³ is identical or different from the other R³ and is each a hydrogen atom, a halogen atom, a C₁-C₁₀ alkyl group which may be halogenated, a C₆-C₁₀ aryl group which may be halogenated, a C₂-C₁₀ alkenyl group, a C₇-C₄₀ - arylalkyl group, a C₇-C₄₀ alkylaryl group, a C₈-C₄₀ arylalkenyl group, a -NR'₂, -SR', -OR', -OSiR'₃ or -PR'₂ radical, wherein R' is one of a halogen atom, a C₁-C₁₀ alkyl group, or a C₆-C₁₀ aryl group;

R⁴ to R⁷ are identical or different and are hydrogen, or are as defined for R³ or two or more adjacent radicals R⁵ to R⁷ together with the atoms connecting them form one or more rings;

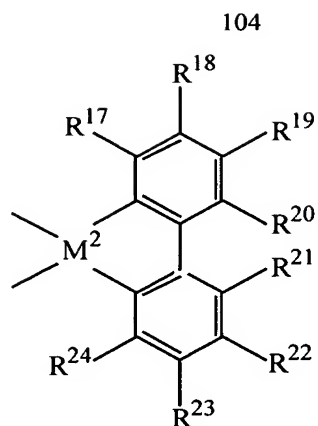
R¹³ is



-B(R¹⁴)-, -Al(R¹⁴)-, -Ge-, -Sn-, -O-, -S-, -SO-, -SO₂-, -N(R¹⁴)-, -CO-, -P(R¹⁴)-, or -P(O)(R¹⁴)-;

wherein: R¹⁴, R¹⁵ and R¹⁶ are identical or different and are a hydrogen atom, a halogen atom, a C₁-C₂₀ branched or linear alkyl group, a C₁-C₂₀ fluoroalkyl or silaalkyl group, a C₆-C₃₀ aryl group, a C₆-C₃₀ fluoroaryl group, a C₁-C₂₀ alkoxy group, a C₂-C₂₀ alkenyl group, a C₇-C₄₀ arylalkyl group, a C₈-C₄₀ arylalkenyl group, a C₇-C₄₀ alkylaryl group, or R¹⁴ and R¹⁵, together with the atoms binding them, form a cyclic ring;

or, R¹³ is represented by the formula:

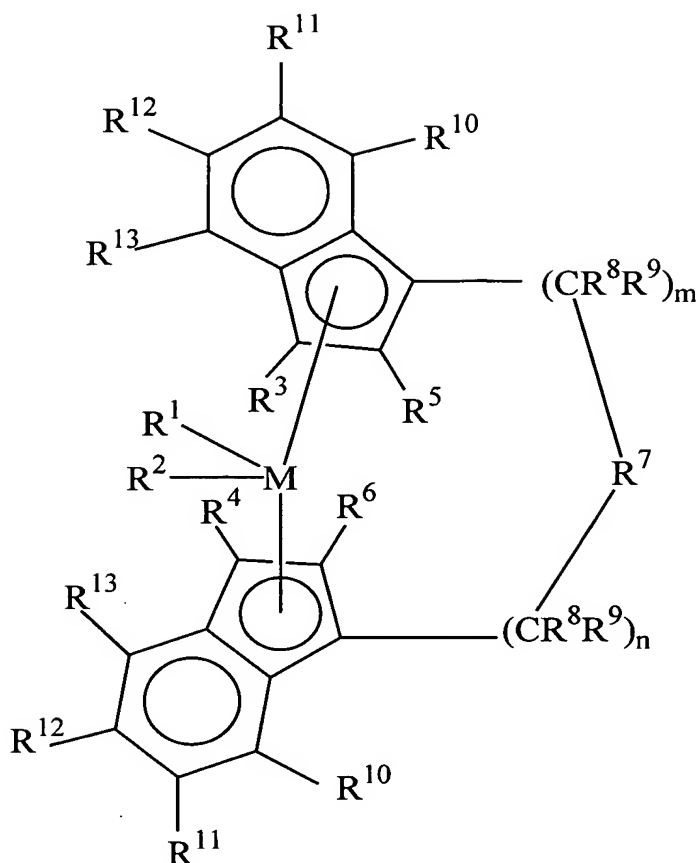


wherein: R^{17} to R^{24} are as defined for R^1 and R^2 , or two or more adjacent radicals R^{17} to R^{24} , including R^{20} and R^{21} , together with the atoms connecting them form one or more rings;

M^2 is one or more carbons, silicon, germanium or tin; and

R^8 , R^9 , R^{10} , R^{11} and R^{12} are identical or different and have the meanings stated for R^4 to R^7 .

23. The process of claim 1, in which the metallocene compound is represented by the formula:



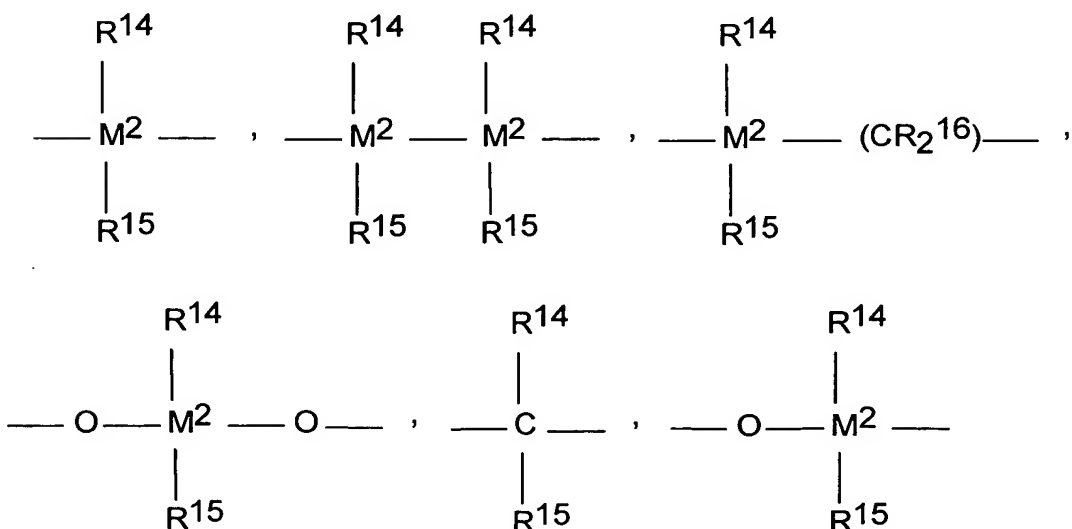
wherein: M is a metal of Group 4, 5, or 6 of the Periodic Table, for example titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten, preferably, zirconium, hafnium and titanium, most preferably zirconium and hafnium;

R^1 and R^2 are identical or different, and are one of a hydrogen atom, a C_1 - C_{10} alkyl group, a C_1 - C_{10} alkoxy group, a C_6 - C_{10} aryl group, a C_6 - C_{10} aryloxy group, a C_2 - C_{10} alkenyl group, a C_7 - C_{40} arylalkyl group, a C_7 - C_{40} alkylaryl group, a C_8 - C_{40} arylalkenyl group, or a halogen atom, or a conjugated diene which is optionally substituted with one or more hydrocarbyl, tri(hydrocarbyl)silyl groups or hydrocarbyl, tri(hydrocarbyl)silylhydrocarbyl groups, said diene having up to 30 atoms not counting hydrogen;

R^3 and R^4 are defined the same as are R^1 and R^2 ;

R^5 and R^6 are identical or different, and are one of a hydrogen atom, a halogen atom, a C_1 - C_{10} alkyl group, which may be halogenated, a C_6 - C_{10} aryl group, which may be halogenated, a C_2 - C_{10} alkenyl group, a C_7 - C_{40} arylalkyl group, a C_7 - C_{40} alkylaryl group, a C_8 - C_{40} arylalkenyl group, a $-NR_2^{15}$, $-SR^{15}$, $-OR^{15}$, $-OSiR_3^{15}$ or $-PR_2^{15}$ radical, wherein: R^{15} is one of a halogen atom, a C_1 - C_{10} alkyl group, or a C_6 - C_{10} aryl group;

R^7 is



$-B(R^{14})-$, $-Al(R^{14})-$, $-Ge-$, $-Sn-$, $-O-$, $-S-$, $-SO-$, $-SO_2-$, $-N(R^{14})-$, $-CO-$, $-P(R^{14})-$, or $-P(O)(R^{14})-$;

wherein: R^{14} , R^{15} and R^{16} are identical or different and are a hydrogen atom, a halogen atom, a C_1 - C_{20} branched or linear alkyl group, a C_1 - C_{20} fluoroalkyl or silaalkyl group, a C_6 - C_{30} aryl group, a C_6 - C_{30} fluoroaryl group, a C_1 - C_{20} alkoxy group, a C_2 - C_{20} alkenyl group, a C_7 - C_{40} arylalkyl group, a C_8 - C_{40} arylalkenyl group, a C_7 - C_{40} alkylaryl group, or R^{14} and R^{15} , together with the atoms binding them, form a cyclic ring;

M^2 is carbon, silicon, germanium or tin;

R⁸ and R⁹ are R⁸ and R⁹, are identical or different, and have the meanings stated for R⁵ and R⁶;

R¹⁰, R¹¹, R¹² and R¹³ are identical or different and have the meanings stated for R⁵ and R⁶; wherein at least one of R¹³ and R¹⁰ are identical or different, and are one of a hydrogen atom, a halogen atom, a C₁-C₁₀ alkyl group, which may be halogenated, a C₆-C₁₀ aryl group, which may be halogenated, a C₂-C₁₀ alkenyl group, a C₇-C₄₀ arylalkyl group, a C₇-C₄₀ alkylaryl group, a C₈-C₄₀ arylalkenyl group, a -NR₂¹⁵, -SR¹⁵, -OR¹⁵, -OSiR₃¹⁵ or -PR₂¹⁵ radical, wherein: R¹⁵ is one of a halogen atom, a C₁-C₁₀ alkyl group, or a C₆-C₁₀ aryl group; and

m and n are identical or different and are zero, 1 or 2, m plus n is zero, 1.

24. The process of claim 1, in which the polymerization medium is substantially gel-free following formation of the polypropylene terpolymer.
25. The process of claim 1, further comprising crosslinking the polypropylene terpolymer.
26. The process of claim 1, in which polymerization medium has less than 90 volume percent diluent.
27. The process of claim 1, in which polymerization medium has less than 50 volume percent diluent.
28. The process of claim 1, in which polymerization medium has less than 30 volume percent diluent.
29. The process of claim 1, in which the final crystalline polypropylene terpolymer is isotactic or syndiotactic.

30. The process of claim 1, in which the metallocene catalyst compound is combined with the monomers in the absence of hydrogen or in the presence of hydrogen in an amount of up to 1.0 mole% hydrogen in the reactor.
31. The process of claim 1, in which the heat of fusion of the crystalline polypropylene is 50 J/g or more.
32. The process of claim 1, in which the heat of fusion of the branched crystalline polypropylene is 70 J/g or more. Add 75 j/g more
33. The process of claim 1, in which the heat of fusion of the branched crystalline polypropylene is 100 J/g or more.
34. The process of claim 1, in which the branched crystalline polypropylene has a Branching Index of 0.98 or less.
35. The process of claim 1, in which the branched crystalline polypropylene has a Branching Index of 0.95 or less.
36. The process of claim 1, in which the branched crystalline polypropylene has a Branching Index of 0.90 or less.
37. The process of claim 1, in which the branched crystalline polypropylene has a Branching Index of 0.80 or less.
38. A polymer composition that includes a branched crystalline diene-modified polypropylene random terpolymer having propylene units; first diene units; second diene units; from 0.0 wt% to 2.0 wt% ethylene units; and a heat of fusion of 30 J/g or more, wherein the first diene units and the

second diene units are derived from different non-conjugated diene monomers, each having 5 or more carbon atoms.

39. The polymer composition of claim 38, in which the random polypropylene terpolymer comprises at least 30% and no more than 95% propylene units; at least 5% and no more than 65% first diene units; at least 0.001% and no more than 2.00% second diene units; and from 0.0 mol% to 3.0 mol% ethylene units.
40. The polymer composition of claim 38, in which the first diene units are derived from α , internal non-conjugated diene monomers.
41. The polymer composition of claim 38, in which the second diene units are derived from α , ω non-conjugated diene monomers.
42. The polymer composition of claim 38, in which the first diene monomer is an α , internal non-conjugated diene monomer that is present in the polypropylene terpolymer in an amount of from 0.0005 mol% to 10 mol%.
43. The polymer composition of claim 38, in which the first diene monomer is an α , internal non-conjugated diene monomer that is present in the polypropylene terpolymer in an amount of from 0.005 mol% to 1 mol%.
44. The polymer composition of claim 38, in which the first diene monomer is an α , internal non-conjugated diene monomer selected from the group consisting of 2-methyl-1,5-hexadiene and 7-methyl-1, 6-octadiene.
45. The polymer composition of claim 38, in which the branched final crystalline polypropylene has a crystallization temperature (T_c) of 50 °C or more.

46. The polymer composition of claim 38, in which the branched crystalline polypropylene has a crystallization temperature (T_c) of 75 °C or more.
47. The polymer composition of claim 38, in which the branched crystalline polypropylene has a crystallization temperature (T_c) of 100 °C or more.
48. The polymer composition of claim 38, in which the branched crystalline polypropylene has a crystallization temperature (T_c) of 110 °C or more.
49. The polymer composition of claim 38, in which the branched crystalline polypropylene has a crystallization temperature (T_c) of from 50°C to 115 °C.
50. The polymer composition of claim 38, in which the branched crystalline polypropylene has a melting point (T_m) of 75 °C or more.
51. The polymer composition of claim 38, in which the branched crystalline polypropylene has a melting point (T_m) of 100 °C or more.
52. The polymer composition of claim 38, in which the branched crystalline polypropylene has a melting point (T_m) of 125 °C or more.
53. The polymer composition of claim 38, in which the branched crystalline polypropylene has a melting point (T_m) of 150 °C or more.
54. The polymer composition of claim 38, in which the branched crystalline polypropylene has a melting point (T_m) of 160 °C or more.
55. The polymer composition of claim 38, in which the branched crystalline polypropylene has a melting point (T_m) of from 75 °C to 160 °C.

56. The polymer composition of claim 38, in which the branched crystalline polypropylene has a melt flow rate of 0.01 or more.
57. The polymer composition of claim 38, in which the branched crystalline polypropylene has a melt flow rate of 0.1 or more.
58. The polymer composition of claim 38, in which the branched crystalline polypropylene has a melt flow rate of 0.5 or more.
59. The polymer composition of claim 38, in which the branched crystalline polypropylene has a melt flow rate of 0.7 or more.
60. The polymer composition of claim 38, in which the branched crystalline polypropylene has a melt flow rate of 1.0 or more.
61. The polymer composition of claim 38, in which the branched crystalline polypropylene has a melt flow rate of 1.5 or more.